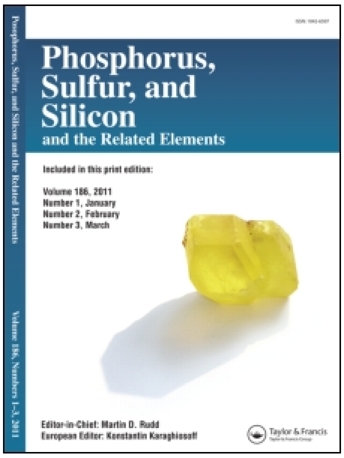

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A NEW TYPE OF SELENIUM HETEROCYCLE: TETRACHLOROBENZO-1,2,3-TRISELENOLE

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A New Type of Selenium Heterocycle: Tetrachlorobenzo-1,2,3-Triselenole

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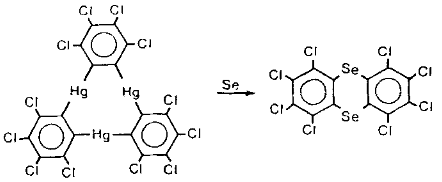
When an excess of selenium is heated with dodecachlorotribenzo[*b,e,h*][1,4,7]trimercuronin in a sealed tube octachlorodibenzoselenanthren and tetrachlorobenzo-1,2,3-triselenole are produced. The bronze-coloured crystals of the triselenole were characterized by elemental and mass spectral analysis.

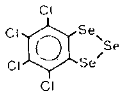
Key words: Dodecachlorotribenzo[*b,e,h*][1,4,7]trimercuronin; perchlorophenylenemercury; tetrachlorobenzo-1,2,3-triselenole; triselenole; octachlorodibenzoselenanthren.

There is currently much interest being shown in unsaturated polychalcogenide heterocycles because many of them display highly unusual electrical properties when incorporated into charge-transfer complexes; for a short introductory review see D Bloor, "Chemistry in Britain", 1983 page 725. We have recently described[1] the preparation of octachlorodiobenzoselenanthren (2) by heating the mercurial (1) and selenium in a sealed tube:

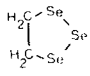


(1) (2)

Further investigation has revealed that tetrachlorobenzo-1,2,3-triselenole is an unexpected by-product of this reaction. As far as we are aware this is the only known aromatic triselenole derivative, although the aliphatic parent (4) was made in 1980.[2]



(3)



(4)

For the success of this synthesis a more convenient source of dodecachlorotribenzo[*b,e,h*][1,4,7]trimercuronin (1) than our original[3] small-scale method was required. Normally mercuric salts, HgX_2, attack aromatic compounds via "mercuration"—the replacement of one or more C—H bonds by C—HgX where X is typically halogen, acetate or trifluoroacetate. However, on attempting to mercurate 1,2,3,4-tetrachlorobenzene with mercuric trifluoroacetate we discovered that a completely unexpected high yield reaction occurs:

$$1,2,3,4\text{—}Cl_4H_2C_6 + Hg(OOCCF_3)_2 \rightarrow \underset{(1)}{(C_6Cl_4Hg)_3} + 6CF_3COOH$$

The product had an identical infrared spectrum to a sample prepared[3] by heating mercury with 1,2-diiodotetrachlorobenzene; both samples showed a parent ion cluster of peaks in their mass spectrum which confirmed a trimeric structure like those of the analogous mercurials $(C_6H_4Hg)_3$[4] and $(C_6P_4Hg)_3$.[5]

Preparation of $(C_6Cl_4Hg)_3$

Mercuric trifluoroacetate was made by heating mercuric oxide (0.06 mol) and trifluoroacetic acid (0.2 mol) under reflux until all the oxide had dissolved; on raising the temperature to about 150° the trifluoroacetic acid distilled off leaving molten $Hg(OOCCF_3)_2$ which was allowed to cool to room temperature and solidify.

The mercuric trifluoroacetate was mixed with an equimolar quantity of 1,2,3,4-tetrachlorobenzene, ground to a fine powder in a mortar and placed in a large test-tube before being heated to about 230° for at least 3 days. (These conditions are obviously not too critical as similar yields have been observed when temperatures between 200° and 280°, with reaction times of 3–7 days, have been used.) Purification of the highly insoluble $(C_6Cl_4Hg)_3$ was accomplished on the large scale by grinding it up to a fine powder and extracting the soluble material in a soxlet apparatus first with hexane and then with toluene. After a final wash with hexane to remove any toluene, the product was dried in air. At this stage the mercurial is sufficiently pure for use in synthetic reactions; analytical samples can be obtained by recrystallisation from either dimethylformamide or nitrobenzene from which solvents the mercurial separates as hemi-solvates.[3] Decomposing these solvates in an oven for some days gives solvent-free material (Found: C = 17.2; H = 0.0; Cl = 34.1%; calculated for $C_{18}Cl_{12}Hg_3$: C = 17.4; H = 0.0; Cl = 34.2%). Yields are 75–80% based on mercuric oxide.

Reaction of $(C_6Cl_4Hg)_3$ *with Selenium*

The mercurial and an approximately three-fold excess of selenium powder were placed in a dry tube which was attached to a vacuum apparatus and pumped down to *ca* 10^{-4} mm Hg pressure before being sealed with a glass-torch at a conveniently placed constriction. The tube was about 300 mm long and of 15–18 mm diameter; two constrictions were provided near to the top end. The tube was sealed at the upper constriction; after the experiment was over a scratch was made on the remaining constriction and the tube, wrapped in a towel, was snapped open. It has been our experience that opening tubes of this diameter by the normal method of "hot spotting" can result in mild explosions—though it is stressed that none have occurred in the work described here.

The tube was placed in a furnace at 350° for one hour when the reaction was judged to be complete. Inspection of the contents when the tube had cooled to room temperature revealed black lumps covered with whisker-like, colourless crystals. After snapping the tube open the contents were extracted first with two 25 ml aliquots of boiling dimethylformamide and then several aliquots of boiling nitrobenzene. The grey solid which rapidly separated from the cooling nitrobenzene extracts was octachlorodibenzoselenanthren.[1]

As the dimethylformamide solutions cooled they deposited a brownish solid which was mainly unused selenium; this was filtered off and the mother liquor set aside for some hours when long, bronze-coloured needles spearated out. These were recrystallized from acetone and dried overnight at 85° (Found: C = 16.2; H = 0.0%; calculated for $C_6Cl_4Se_3$: C = 16.0; H = 0.0%); melting point 179°. A mass spectrum of the triselenole showed a group of isotopomeric peaks around mass 452 corresponding to the parent ion $C_6Cl_4Se_3^+$. The base peaks in the spectrum were around mass 160 due to the ion Se_2^+; other intense and important ions present were $C_6Cl_4Se_2^+$, $C_6Cl_4Se^+$, $C_6Cl_3Se_2^+$, $SeCl^+$ and Se^+. A high resolution study of the cluster of peaks around mass 452 confirmed that they belonged to the parent ion:

measured mass	calculated mass	isotopomer
447.629	447.627	$\mathrm{C_6{}^{78}Se_2{}^{80}Se^{35}Cl_4}$
449.627	449.626	$\mathrm{C_6{}^{78}Se^{80}Se_2{}^{35}Cl_4}$
451.625	451.625	$\mathrm{C_6{}^{80}Se_3{}^{35}Cl_4}$
453.623	453.622	$\mathrm{C_6{}^{80}Se_3{}^{35}Cl_3{}^{37}Cl}$
453.627	453.625	$\mathrm{C_6{}^{80}Se_2{}^{82}Se^{35}Cl_4}$
455.624	455.619	$\mathrm{C_6{}^{80}Se_3{}^{35}Cl_2{}^{37}Cl_2}$

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